Model-based analysis of anion-exchanger positioning in direct methanol fuel cell systems

Maik Kraus [b], Daniel Schröder [a], Ulrike Krewer [a,b,*]

[a] Institute of Energy and Process System Engineering, TU Braunschweig, Franz-Liszt-Str. 35, 38106 Braunschweig, Germany
[b] Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, 39106 Magdeburg, Germany

HIGHLIGHTS

- We studied the impact of carbon dioxide on the design of active portable DMFC systems with a model-based approach.
- It is discussed how the concentration of carbon species is effected by methanol concentration in methanol−water-solution.
- The amount of carbon species in dependency of the temperature and partial pressure is presented.
- Study of the position and design of the anion exchanger in the anode loop under the aspect of portability.
- Influence of the gas liquid separator design on carbon species concentration is presented.

ABSTRACT

In this work we present a model based study to investigate the presence of anion exchangers in direct methanol fuel cell (DMFC) systems. It is well known that environmental or fuel impurities lead to accumulation of harmful anions, such as chloride, in the system. However, due to DMFC anodic reaction, a carbonate system is present. These corbanate anions have to be taken into account for the anion exchanger design and placement as well as for the system operation strategy with and without anion exchanger, which is the objective of this study. For this purpose, the expected amount of harmful chloride ions in a DMFC system is estimated, and that of carbonate ions is calculated with a model of the carbonate system in a DMFC system. The predicition of durability and dimensions of an anion exchanger is based on a monovalent anion exchange model. The design of gas liquid separators in the DMFC system has a major influence on the amount of dissolved carbon dioxide, which is crucial for durability and dimension of a system integrated anion exchanger. Finally, feasible positions of anion exchanger in a DMFC system are elaborated to fulfill the needs for long term and stable DMFC operation.

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1. Introduction

Direct methanol fuel cell (DMFC) systems are attractive energy sources for portable appliances. In order to prevent DMFC degradation, the accumulation of ionic species in the DMFC system from various sources should be avoided, as they negatively affect DMFC system performance [1–4]. Specifically, Cl^- enters the system as an impurity in fuel cell components, such as catalyst layer or membrane, or as a pollutant in the charged air. Due to water recovery from the cathode side and the presence of NH_4Cl in the supplied air [3], an enrichment of Cl^- in the anode loop is possible. Besides, an enrichment of metal and non-metal ions in the anode solution and in the membrane electrode assembly (MEA) of the DMFC was found to cause significant performance issues [5].

To avoid the before mentioned accumulation of harmful ionic impurities in the anode loop, including anion exchangers into the DMFC system has been proposed [5]. However, the application of anion exchangers in DMFC systems is strongly influenced by the DMFC system itself. Due the production of CO_2 in the DMFC anode reaction, CO_2 dissolves and forms carbonate species such as hydrogen carbonate (or bicarbonate), HCO_3^-, and carbonate ions, CO_3^{2-} [6,7]. In a DMFC system with an anion exchanger in the anode loop, these anionic carbon species rival with anions from impurities

* Corresponding author. Institute of Energy and Process System Engineering, TU Braunschweig, Franz-Liszt-Str. 35, 38106 Braunschweig, Germany. Tel.: +49 531 391 3030; fax: +49 531 391 5932.
E-mail addresses: maik.kraus@googlemail.com (M. Kraus), da.schroeder@tu-braunschweig.de (D. Schröder), u.krewer@tu-braunschweig.de (U. Krewer).

for the ion exchange and can therefore determine the durability and dimension of the applied anion exchanger.

In this paper, we evaluate the feasibility of an anion exchanger and its placement in a DMFC system. First we estimate the amount of harmful ions like Cl^- as well as the amount of carbonate species which occur at different positions in the DMFC system. This is done by means of a systematic investigation of the present carbonate system in the DMFC system. A model based approach is applied to account for the amount of dissolved carbonate species as a function of operating parameters of the fuel cell, such as temperature and methanol concentration. Secondly, a monovalent anion exchanger model is set up and charged with different flow rates of solution containing varying concentrations of before mentioned anions to determine its durability and dimensions. As a result, we show that, depending on the gas phase above the solution, carbonate systems occur in the DMFC system: the semi-open carbonate system is expected in the gas liquid separator, whereas the closed carbonate system exists in the DMFC anode compartment and all other parts of the anode loop, especially in the anion exchanger. The occurrence of different carbonate systems influences the position of the anion exchanger. Based on these results, we demonstrate which anion exchanger positions in the DMFC system are feasible to fulfill the needs for long term and stable operation.

2. Methods and preliminary considerations

In the following section, the expected amount of ion species of chloride and carbonate ions is estimated and the essential model equations for this work are derived. The DMFC system considered in this work is sketched in Fig. 1. It consists of the DMFC, the gas liquid separator at the anode side, the liquid gas separator at the cathode side, the methanol supply with methanol tank and fuel pump, and the respectively placed anion exchanger in the anode loop.

Expected amount of chloride impurities. Chloride ion impurities can enter the DMFC anodic loop via the neat methanol solution used, which possesses a given chloride impurity of 0.5 ppm that results in 1×10^{-5} mol l^{-1} Cl^- for 1 M methanol solution. Another source of chloride ions is the liquid gas separator behind the DMFC cathode compartment where product water is recycled and fed back to the anodic loop. Due to the usage of atmospheric oxygen the concentration of methyl chloride (CH_3Cl), which is the most abundant halocarbon in the atmosphere and therefore the most important source for chloride anions, reaches average values of approximately 500 ppt [3]. Due to the very low solubility of chloride in water [8], we estimate a concentration of 2×10^{-7} mol l^{-1} dissolved Cl^- for this work.
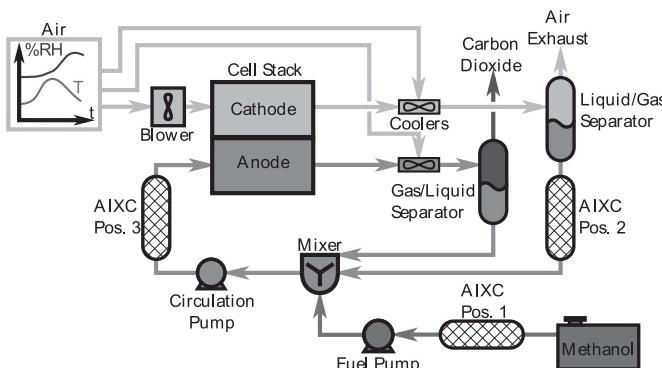
Fig. 1. Schematic of the DMFC system with different options for positioning the anion exchanger. The DMFC system is described in more detail elsewhere [23].

2.1. Expected amount of carbonate ion species

If gaseous CO_2 is in contact with an aqueous solution, it partly dissolves in the solution and a carbonate system evolves. In the following, we give a brief introduction on the carbonate system and investigate its appearance in DMFC systems.

Dissolved CO_2 yields three different inorganic species in aqueous solutions: dissolved carbon dioxide, $CO_2(diss)$; bicarbonate, HCO_3^-; and carbonate ion, CO_3^{2-}. All together constitute the carbonate system [6] and their individual concentrations are related as follows:

$$[CO_2(diss)] \equiv H_{CO_2}^* \cdot p'_{CO_2} \tag{1}$$

$$\left[H^+\right] \cdot \left[HCO_3^-\right] = [CO_2(diss)] \cdot K_{a1} \tag{2}$$

$$\left[H^+\right] \cdot \left[CO_3^{2-}\right] = \left[HCO_3^-\right] \cdot K_{a2} \tag{3}$$

$$\left[H^+\right] \cdot \left[OH^-\right] = K_W \tag{4}$$

where concentrations in liquid phase are indicated with square brackets and the unit of $H_{CO_2}^*$, Henry's law coefficient, is mol l^{-1} [9]. K values indicate the pressure and temperature dependent dissociation constants. K_W is referred to as the ion product of water. The respective constants used in the present work are given in Table 1.

Consequently, the carbonate system is described completely with the use of Equations (1)–(4), the sum of all dissolved carbon dioxide species (DIC) (5) and the electroneutrality condition (6):

$$DIC = \left[HCO_3^-\right] + \left[CO_3^{2-}\right] + [CO_2(diss)] \tag{5}$$

$$0 = \left[H^+\right] - \left[HCO_3^-\right] - 2 \cdot \left[CO_3^{2-}\right] - \left[OH^-\right] \tag{6}$$

The influence of methanol on the dissolution of carbon dioxide is given by Ref. [13]. Since, a highly diluted methanol water solution is expected at the anode outlet, the influence of methanol on the carbonate system can be neglected for DMFC operation. This accompanied by considering the methanol influence on Henry's law coefficient for the carbonate system as described in Section 2.2.

Depending on the properties or existence of a gas phase above a solution, the carbonate system can be classified as open (a), closed (b) or semi-open (c) carbonate system [6]. The open system is the most complex, as found e.g. in sea water systems in contact with environmental air. We consider it as not relevant for DMFC operation. The semi-open system possesses a gas phase with a constant amount of gaseous carbon dioxide with a constant partial pressure p'_{CO_2} as it may occur in certain parts of the DMFC system. The closed system possesses no gas phase above the solution that interacts with the environmental atmosphere. A schematic representation of the carbonate systems used in this work, is depicted in Fig. 2. In the same figure, an overview on the expected amounts of carbonate species is given for the closed carbonate system and the semi-open carbonate system. The minimal depicted partial pressure is set to the expected partial pressure of carbon dioxide in the atmosphere of about 3.535×10^{-5} MPa, whereas the maximal depicted partial pressure is equal to atmospheric pressure of 0.101325 MPa at 298 K. According to $p'_{CO_2} = 0.101325$ MPa given by the anode side gas liquid separator, the aqueous methanol solution will be present with a maximal possible concentration of dissolved carbonate of $c_{CO_2(diss)} = 2.26 \times 10^{-2}$ mol l^{-1}. Table 2 lists all relevant DMFC

Table 1
Equilibrium constants used in this work reference.

Constant	Expression	Unit	Reference
H_{CO_2}	$\exp\left(-6.8346 - \frac{12817}{T} - \frac{3766800}{T^2} + \frac{299700000}{T^3}\right)$	MPa	[10]
K_{a1}	$\exp\left(-356.3094 - 0.06091964\,T + \frac{21834.37}{T} + 126.8339\log(T) - \frac{1684915}{T^2}\right)$	mol l^{-1}	[11]
K_{a2}	$\exp\left(-107.8871 - 0.032528493\,T + \frac{5151.79}{T} + 38.92561\log(T) - \frac{563713.9}{T^2}\right)$	mol l^{-1}	[11]
K_W	$\exp\left(21.6470 - \frac{4239.4000}{T} - 3.7546\log(T)\right)$	mol^2 l^{-2}	[11], respectively [12]

components, indicated with the respective carbonate systems as they might appear in DMFC systems.

2.2. Model of DMFC anode compartment

In the following, a steady state model for the DMFC anode loop, as illustrated in Fig. 1, containing an anion exchanger at different positions is presented. It consists of a DMFC anode compartment model and models for the other anodic loops parts to describe the expected amount of carbon species in each part depending on DMFC operating conditions. The DMFC anode compartment model consists of mass balances describing the liquid and gaseous species.

It is assumed that the considered DMFC operates at a temperature T_{FC} and atmospheric pressure p_{atm}. The molar flow rate of produced carbon dioxide is equal to the molar flow rate of methanol needed for the DMFC anode reaction. According to Faraday's law, it follows:

$$\dot{n}_{Me,need} = \frac{I \cdot N_{cell}}{6 \cdot F} = \dot{n}_{CO_2,prod} \tag{7}$$

Knowing that methanol is fed with excess by the factor of λ_{Me}, the molar flow rate of methanol entering the anode is:

$$\dot{n}_{Me,in} = \lambda_{Me} \cdot \dot{n}_{Me,need} \tag{8}$$

Therefore, the volumetric flow rate of fed methanol from the fuel pump is expressed by:

$$F_{Me} = \frac{\dot{n}_{Me,need} \cdot M_{Me}}{\rho_{Me}(T_{cool})} \tag{9}$$

The density of methanol ρ_{Me} is determined with data by Lide [14].

The molar flow rate of solution $\dot{n}_{feed}$ entering the anode is the sum of the molar flow rates of methanol and water:

$$\dot{n}_{feed} = \dot{n}_{Me,in} + \dot{n}_{H_2O,in} \tag{10}$$

Due to the fact that the system is fed with a diluted water methanol solution (<3 wt %), the volumetric flow rate of solution entering the anode F_{feed} is approximated by:

Fig. 2. The carbonate system and a) its classification according to Stumm and Morgan [6]; b) the concentration of the ionic species for a closed carbonate system at 1 atm and 298 K and for semi-open conditions: c) versus partial pressure range and d) versus temperature range.

Table 2
Assignment of classification of the carbonate system to relevant DMFC components.

Component	Type
DMFC (anode compartment)	Closed
Cooler	Closed
Separator	Semi open
Mixer	Closed
Circulation Pump	Closed

$$F_{\text{feed}} = \frac{\dot{n}_{\text{feed}} \cdot M_{\text{feed}}}{\rho_{\text{feed}}(T_{\text{cool}})} \approx \frac{\dot{n}_{\text{feed}} \cdot M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}(T_{\text{cool}})} \tag{11}$$

where it is assumed that the density and the molar mass of the diluted methanol water solution possesses about the same density as pure water [15]. The density of water is calculated with an empirical equation [16].

Furthermore, the molar amount of solution lost in the anode compartment is the sum of lost methanol and water due to cross-over from anode to cathode compartment and anode reaction (subscript xover and reaction, respectively), and the molar flow rate of solution exiting the anode compartment is denoted as $\dot{n}_{\text{out}}$. Considering this, it follows:

$$\dot{n}_{\text{out}} = \dot{n}_{\text{feed}} - \dot{n}_{\text{Me,reaction}} - \dot{n}_{\text{Me,xover}} - \dot{n}_{\text{H}_2\text{O,reaction}} - \dot{n}_{\text{H}_2\text{O,xover}} \tag{12}$$

Thereby, the terms of reaction for water and methanol are stoichiometrically expressed by Equation (8). Water crossover is accounted for with a water drag coefficient k [17]:

$$\dot{n}_{\text{H}_2\text{O,xover}} = k \cdot \frac{I \cdot N_{\text{cell}}}{6 \cdot F} \tag{13}$$

Methanol influences the equilibrium constant of the gas liquid interaction between carbon dioxide and the solution, and it impacts the dissociation of the carbonate system species. A vast set of experimental data for Henry's law constants in pure water systems was previously investigated [10,11], presenting temperature dependent correlations valid for atmospheric pressure. The impact of methanol concentration on Henry's law constants for methanol water solutions with CO_2 is given in literature [13]. A comparison of Henry's law constants with and without methanol influence is given in Appendix B. Henry's law constants from the above mentioned authors are plotted as function of temperature in Fig. B.1. It has to be noted that the given Henry's law constants are converted to MPa units to ensure comparability [9].

Methanol crossover is neglected for this study, as the difference in concentration will not effect the solubility of CO_2, compare Fig. B.1, so that $\dot{n}_{\text{Me,xover}} = 0$. Finally, this results in:

$$\dot{n}_{\text{out}} \approx \left(\frac{\lambda_{\text{Me}}}{x_{\text{Me}}} - 2 - k\right) \cdot \frac{I \cdot N_{\text{cell}}}{6 \cdot F} \tag{14}$$

where x_{Me} represents the molar fraction of methanol in the liquid phase which depends on the molar concentration of methanol and water in the anode feed solution.

Assuming the same conditions as in Equation (11), the volumetric flow rate of the liquid phase is approximated by:

$$F_{\text{out}} \approx \frac{\dot{n}_{\text{out}} \cdot M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}(T_{\text{cool}})} \tag{15}$$

With Equations (7) and (14), the molar flow of gas and liquid exiting the anode and entering the cooler, and consequently the gas liquid separator, can be described. The anode cooler is not described separately, but determines the operating temperature for the gas liquid separator with its temperature T_{cool}.

The dissociation reactions in the carbonate system (Equations (2)–(4)) take place in the range of 10^{-2} s and 10 s [18]. The slowest process is the dissolution, Equation (1) [6]. We assume the residence time of the methanol water solution in all system components of the given standard DMFC system to be sufficient to obtain thermodynamic equilibrium regarding the carbonate system.

2.3. Possible positions of the anion exchanger

The DMFC system considered in this work, as sketched in Fig. 1, operates at constant current and in steady state. This implies that a constant volumetric flow of solution enters and leaves each component in the anode loop, e.g. the gas liquid separator. Furthermore, the gas liquid solution is assumed to be in thermodynamic equilibrium regarding the carbon dioxide species with its dissolved species.

At position 1, the anion exchanger is investigated at the methanol tank outlet fed with constant chloride impurity and a volumetric flow rate F_{Me} according to a set DMFC system steady state. The given chloride impurity by the manufacturer of 0.5 ppm results in about 1×10^{-5} mol l^{-1} Cl$^-$ in the pure methanol solution. For the anion exchanger at position 2, the water regained from the cathode side is saturated with CO_2 with environmental partial pressure of carbon dioxide of 3.535×10^{-5} MPa. This results in a concentration of [CO_2(diss)] $\approx 1 \times 10^{-5}$ mol l^{-1} in the recycled water. At position 3, the anion exchanger is considered to be at the anode compartment inlet fed with F_{feed} containing dissolved carbon dioxide $c_{\text{CO}_2(\text{diss})}$ and Cl$^-$. An anion exchanger at this position has the task to remove all harmful anionic impurities completely. However, the expected concentration of carbonate species anions is marginally higher then for example the Cl$^-$ concentration at this position.

2.4. Anion exchanger model

The considered anion exchanger is a column filled with anion exchange resin particles. In the following we assume an ideal monovalent anion exchange of two kinds of anions: either HCO$_3^-$, originating from the carbonate system, or Cl$^-$, exemplary for impurities. The anion exchange column is fed with a volumetric flow rate from the DMFC system containing the anions A and B, where A is the anion which is intended to be exchanged, as HCO$_3^-$ or CO$_3^{2-}$ or Cl$^-$, respectively. Anion B is considered to be OH$^-$ and is already loaded onto the resin particles. Furthermore, the packed resin particles are equally distributed possessing a uniform particle size. Mass transfer resistance in the macro pores of the resin and axial dispersion in the packed column as well as possible back flows inside the column are neglected.

In a DMFC, the present ionic species is HCO$_3^-$ rather than CO$_3^{2-}$. We therefore consider solely HCO$_3^-$ as the ion which will be intentionally removed from a solution passing the anion exchanger.

If the anion exchange resin particles are completely loaded with ion HCO$_3^-$ or CO$_3^{2-}$ or Cl$^-$, respectively, it is considered to be full and the durability of the anion exchanger is reached.

To determine the durability of the anion exchanger, a model for anion exchange (AIXC) columns is formulated. It combines an ideal plug flow model with the estimation of a local anion exchange equilibrium according to an equilibrium isotherm [19]. The anion exchanger durability is the ratio of column dimensions and propagation velocity of the ion species A inside the column:

$$t_{\text{AIXC}} = \frac{L \cdot \frac{\pi}{4} \cdot D^2 \left(\varepsilon + (1-\varepsilon) \cdot \frac{Q}{c_{\text{A,in}}}\right)}{F_{\text{IE}}} \tag{16}$$

Table 3
Reference operating conditions at steady state for DMFC operation and anion exchanger parameter.

Operating parameter	Value	Unit
$p_{atm} = p'_{CO_2}$	0.101325	MPa
T_{FC}	333	K
T_{cool}	310	K
N_{cell}	1	–
I	3.5	A
λ_{Me}	3	–
c_{Me}	1	mol l^{-1}
k	0	–
D	4	mm
L	40	mm
ε	0.4	–
Q	0.8	mol l^{-1}

The inter particle porosity of the anion exchanger resin in Equation (16) is expressed by ε and constant volumetric flow and concentration $c_{A,in}$ and a low concentration $c_{B,in}$ in the fed solution are assumed.

All subsequently presented calculations for the anion exchanger durability are calculated with the chosen reference operating conditions given in Table 3.

3. Results and discussion

In the following section, we present the results of the model based analysis and elucidate the anion exchanger lifetime according to its placement in the DMFC system. It was shown in the previous section that the concentration of carbonate species is much higher then the concentration of impurities in the system. Therefore, we first estimate the durability of the anion exchanger solely for Cl$^-$ and then solely for the presence of HCO$_3^-$.

3.1. Anion exchanger durability based on chloride impurities

For the three different possible positions of the anion exchanger in the DMFC anode loop the resulting anion exchanger lifetimes are given in Table 4. At position 1, the anion exchanger is investigated at the methanol tank outlet fed with $F_{Me} = 15.04$ µl min^{-1} at chosen reference conditions and a low chloride concentration, this results in high anion exchanger durability. At position 2, behind the liquid gas separator on the cathode side, we assume the dissolved amount of chloride to be much lower than the amount of dissolved carbon dioxide due to the very low solubility of chloride in water [8]. Consequently, while Cl$^-$ will also be removed, solely carbonic anions are considered to determine the lifetime of an anion exchanger at this position (see next subsection). At position 3, the anion exchanger is considered to be at the anode compartment inlet fed with F_{feed} containing dissolved carbon dioxide $c_{CO_2(diss)}$ and Cl$^-$. An anion exchanger at this position has the task to remove all anionic impurities completely. Assuming that the anions are caused by the impurities of the refreshed methanol solution, the Cl$^-$ concentration is approximated as 2×10^{-7} mol l^{-1}. This results in an anion exchanger durability for chloride of about 3 years, which is a suitable lifetime compared to other DMFC system components.

3.2. Anion exchanger durability based on carbonate ions

In addition to the chloride impurities also carbonate ions are present in the anode loop due to the reaction of methanol and water in the anode compartment of the DMFC. Depending on the position in the loop, the anion exchanger will be fed with a different amount of carbonate ions. For the positions given in Fig. 1, the resulting anion exchanger durability are presented in Table 5. At position 1, the anion exchanger is investigated at the methanol tank outlet, where we expect only pure methanol without carbonates to be applied. Consequently the carbonate ion concentration and other impurities than chloride in the methanol solution are neglected at this position. For the anion exchanger at position 2, the water regained from the cathode side is saturated with CO$_2$ with environmental partial pressure of carbon dioxide of 3.535×10^{-5} MPa. In real DMFC operation this value can even be higher due to the methanol crossover, as CO$_2$ is produced in a side-reaction [20] and the partial pressure will be higher than the environmental partial pressure.

The volumetric flow rate of the recycled water is given by the reaction ($\dot{n}_{H_2O,reaction}$) as well as by the water crossover ($\dot{n}_{H_2O,xover}$), and with $k = 10$ it is 7.30 µl min^{-1}. Therefore the durability of the anion exchanger is 0.69 years, if all ionic carbon species are removed. The long durability is mainly due to the very low flow rate of recycled water and can be considered feasible for portable DMFC systems. At position 3, the anion exchanger is considered to be at the anode compartment inlet fed with $F_{feed} = 1.10$ ml min^{-1} at standard operating conditions. According to $p'_{CO_2} = 0.101325$ MPa given by the anode side gas liquid separator, the methanol solution contains the maximal possible concentration of $c_{CO_2(diss)} = 2.26 \times 10^{-2}$ mol l^{-1}. This results in an anion exchanger durability of about only 0.144 h. Since, dissolved carbon dioxide has the main influence on the anion exchanger durability at position 3, durability might not be suitable for portable DMFC system operation.

Another way to influence the amount of dissolved carbon dioxide is given by the design of the gas liquid separator in the anode loop of the DMFC system. The H$^+$ concentration and the pH value in the anode loop are mainly determined by the partial pressure of carbon dioxide in the gas phase. To illustrate the latter, Fig. 3 shows the pH value in the semi-open carbonate system as a function of system temperature and partial pressure of carbon dioxide. Thereby, the minimal pH value is 3.90, depicted in the bottom corner at maximal partial pressure and minimal system temperature. By implication, pH = 5.75 in the upper corner is assigned to minimal partial pressure and maximal system temperature. The pH value at constant partial pressure changes only slightly as function of temperature, for example at $p'_{CO_2} = 0.101325$ MPa from pH 3.9060 to 4.0940.

This implies for the cooler and the gas liquid separator operation that a change in operating temperature does not change the pH value significantly. Consequently, the design of a gas liquid separator in a DMFC (compare Fig. 3 1) and 2)) might be considered solely regarding the pressure of carbon dioxide. Assuming an application of a micro separation unit, as presented by Kraus et al. [21], a significant higher pH value, which corresponds to a lower concentration of dissolved carbonate ions, is expected at the unit outlet. This is due to the fact that the liquid phase in this unit has direct contact with the environmental air. Therefore the design of

Table 4
Calculated anion exchanger lifetimes depending on the concentration of chloride ions at the corresponding position in the DMFC anode loop.

Position	Expected concentration mol l^{-1}	Anion exchanger lifetime
1)	1×10^{-5}	2.5 years
2)	≈ 0	$\approx \infty$
3)	2×10^{-7}	3 years

Table 5
Calculated anion exchanger durability depending on the concentration of carbonate ions at the corresponding position in the DMFC anode loop.

| Position	Expected concentration mol l^{-1}	Anion exchanger durability
1)	≈ 0	$\approx \infty$
2)	$\approx 1 \times 10^{-5}$	0.69 years
3)	2.26×10^{-2}	0.144 h
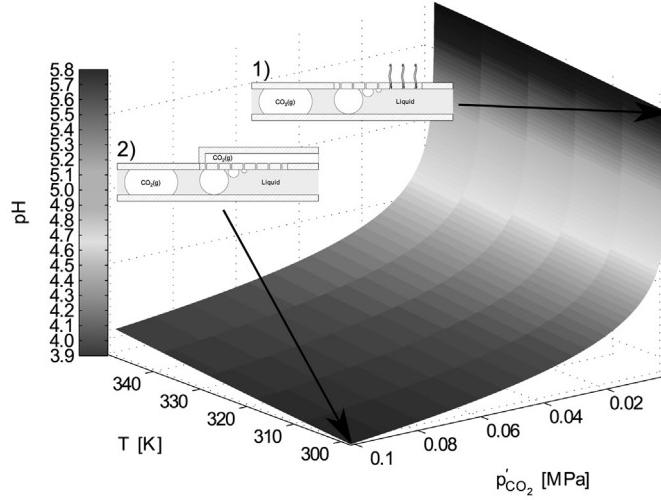
Fig. 3. pH value in the semi-open carbonate system as function of temperature and partial pressure of carbon dioxide. The design of the semi-open, capillary-based gas liquid separators [21] with 1) an open separation area, where the degassed methanol solution stays in contact with environmental air, and 2) a covered separation area, where CO_2 gas is accumulated up to the environmental pressure of 1 bar.

micro channel based separation units can have a major influence on the amount of the carbonic anion species in DMFC systems.

3.3. Dimension of anion exchanger depending on system and design

According to Equation (16), clear trends to specify the anion exchanger durability are observed. Increasing the column length L and the anion exchange capacity Q increases the anion exchanger durability linearly. Extending the column diameter D increases the anion exchanger durability quadratically. An increase in inter

particle porosity ε decreases the anion exchanger durability linearly. Since portable operation favors a reduction of column dimensions, the column diameter D is an appropriate way to scale the anion exchanger durability. Fig. 4a)–d) shows the influence of selected DMFC system and anion exchanger design parameters on the predicted anion exchanger durability, when it is placed directly in front of the DMFC anode inlet at position 2. Thereby all parameters are set to the chosen reference conditions from Table 3, except the respective investigated parameter. Fig. 4a) to b) depict the results for parameters which are related to the flow rate in the anode loop. I and
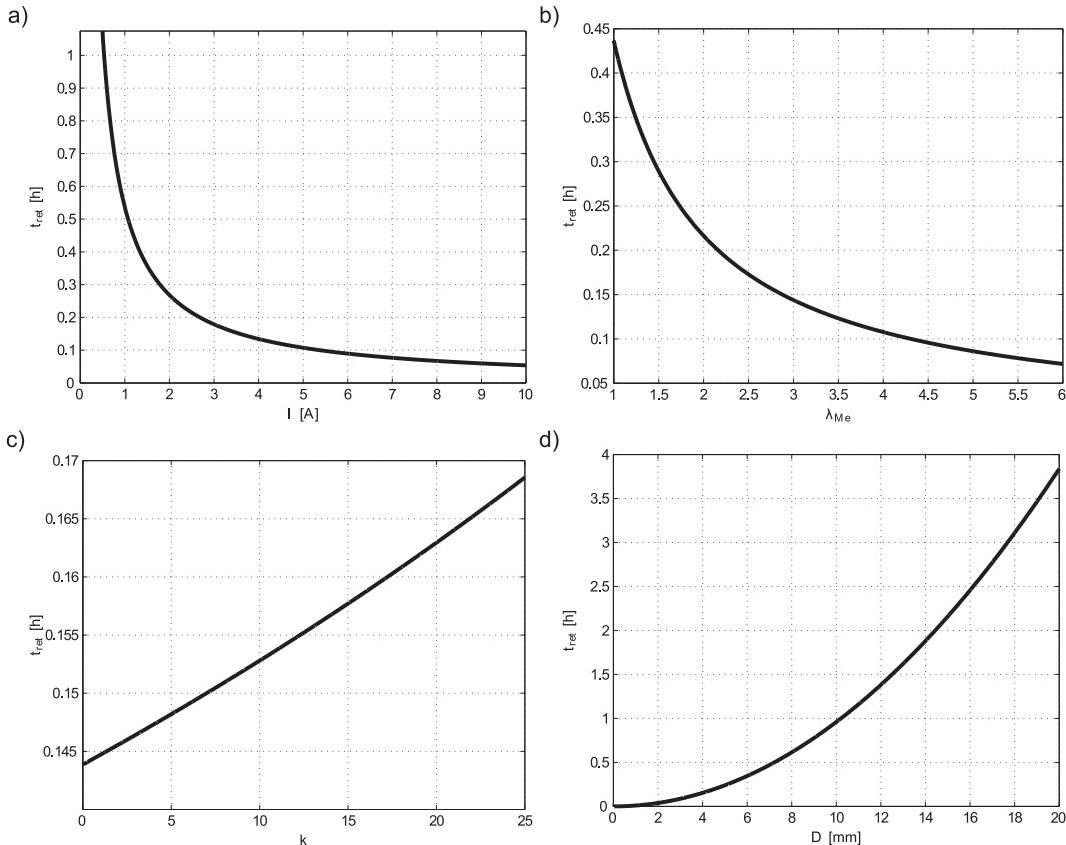
Fig. 4. Anion exchanger durability t_{ret} as function of: a) fuel cell current, b) methanol excess ratio λ_{Me}, c) water drag coefficient k and d) column diameter D.

λ both increase with F_{Feed} and as such show reciprocal influence on the anion exchanger durability.

As presented in Fig. 4c), the water drag k invokes only a slight and almost linear influence on anion exchanger durability. This can be explained by water moving to the cathode which decreases $\dot{n}_{out}$, and as such the total amount of carbon dioxide which is taken up by the solution. This solution is then diluted in the mixer with recovered water from the cathode condenser which contains a significant lower amount of ionic carbon species.

Fig. 4d) depicts exemplary one result for anion exchange column design parameters, the column diameter. Compared to the impact of DMFC operating system parameters, the column diameter influences the anion exchanger durability stronger.

4. Conclusions

In this paper, model based investigations of the carbonate system and anion exchangers in a DMFC system are presented. It is shown, that anions are not exclusively present in the DMFC system due to environmental or methanol impurities but rather by the electrochemical CO_2 production at the anode compartment and the consequently evolving carbonate system. For the removal of anions, the usage of an anion exchanger at different positions and design in the DMFC system is considered.

If the accumulation of harmful anions like chloride in the anode loop and consequently DMFC degradation is occurring, anion exchangers are a suitable tool to implement in DMFC systems. We have shown by a model based analysis that only certain positions in the DMFC system are practical for example for portable operation: a position directly in front of the anode inlet is not suitable for portable applications because carbonate ions outnumber any impurities by far and as such lead to very low anion exchanger durability. The position behind the methanol tank as well as the position in the recycling line offer suitable lifetimes and anion exchanger sizes for a portable usage.

Regarding the carbonate system in a DMFC, the methanol influence can be neglected within the expected operation range. Furthermore, the concentrations of carbonate species and pH values are mainly influenced by the partial pressure of carbon dioxide the solution has been exposed to, rather than by the system temperature. Hence, gas liquid separators are key factors in DMFC systems regarding the carbonate ion concentration and the water balance of portable DMFC systems. This complements the above mentioned findings [21,22], where separators are considered as key parts of DMFC system design. To achieve long term and stable operation, considering carefully the gas liquid separators as well as anion exchangers will be necessary for DMFC system design.

Appendix A. Calculation of the semi-open and closed carbonate system

Appendix A.1 Semi-open system

To determine the concentration of dissolved carbon dioxide $[CO_2(diss)]$ in the semi-open system, Henry's law is combined with the respective law of mass action. Thereby, Henry's law is valid for a system pressure below 0.5 MPa and assumes ideal dilute solution behavior. Usually, Henry's law constant H is defined as the ratio of the concentration of a species in the solution phase c and the partial pressure p' of the species in the gas phase:

$$H = \frac{c}{p'} \tag{A.1}$$

With this definition the unit of H is $mol\,l^{-1}\,MPa^{-1}$. However, values for H are expressed in literature in several ways using different units

according to modified equations of Henry's law. Sander [9] gives a detailed review on used Henry's law constants and their unit conversions.

To calculate the species concentrations the law of mass action is applied to the equilibrium reactions, which leads to Equations (1)–(4). With Equations (5) and (6) in mind, six equations for the seven unknown concentrations $[CO_2(g)]$, $[CO_2(diss)]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$, $[OH^-]$ and DIC with given temperature and system pressure are obtained. As a consequence, one unknown is additionally needed to calculate the remaining species concentrations. Usually, $[CO_2(g)]$ is given by the partial pressure of carbon dioxide p'_{CO_2} in the gas phase above the solution of about 3.535×10^{-5} MPa in the atmosphere according to Ref. [7]. Rearranging the set of equations, yields to a third order equation for $[H^+]$ as a function of the known value p'_{CO_2} and the equilibrium constants:

$$0 = \left[H^+\right]^3 - \left(K_W + K_{a1} \cdot H_{CO_2} \cdot p'_{CO_2}\right) \cdot \left[H^+\right] \\ - 2 \cdot K_{a1} \cdot K_{a2} \cdot H_{CO_2} \cdot p'_{CO_2} \tag{A.2}$$

whereas it is important that Henry's law constant is denoted with $mol\,l^{-1}\,MPa^{-1}$ and p'_{CO_2} with MPa. Only the one non-complex solution of the three solutions of Equation (A.2) is physically meaningful and yields the pH value as the concentration of H^+. Consequently, the semi-open system can be validated by measuring the pH value at given temperature and system pressure.

Appendix A.2 Closed system

No gas phase is present and the reaction (A.3) is not existent in this system.

$$CO_2(g) \overset{H^*_{CO_2}}{\rightleftharpoons} CO_2(diss) \tag{A.3}$$

Consequently, five equations for the six unknown concentrations $[CO_2(diss)]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[H^+]$, $[OH^-]$ and DIC with given temperature and system pressure are remaining. Again, one unknown is additionally needed to calculate the remaining species concentrations. Thereby, the unknown concentration can be seen as entering the system inlet determining the other species concentrations according to the thermodynamic equilibrium.

There are six possibilities to calculate the carbon system species concentrations in a closed system [7]. As example, the result for calculating with known DIC is shown. Combining the equations mentioned above leads to $[H^+]$ as a function of DIC and the equilibrium constants:

$$0 = \left[H^+\right]^4 + K_{a1} \cdot \left[H^+\right]^3 + (K_{a1} \cdot K_{a2} - K_W - K_{a1} \cdot DIC) \cdot \left[H^+\right]^2 \\ + (-2 \cdot K_{a1} \cdot K_{a2} \cdot DIC - K_{a1} \cdot K_W) \cdot \left[H^+\right] - K_{a1} \cdot K_{a2} \cdot K_W \tag{A.4}$$

In general, fourth order equations like Equation (A.4) have four solutions. Only one of it is physically meaningful. With it, the remaining species concentrations can be determined according to the set of equations. Again, the concentration of H^+ yields the pH value and consequently the closed system can be determined by measuring the pH value. In the limiting case of DIC becoming zero, the pH is approximately 7, hence only water is present in the system. Besides, this case is equal to a semi-open system with p'_{CO_2} becoming zero.

Appendix B. Methanol in the carbonate system

We elucidate the influence of methanol on the evolved carbonate system in a DMFC and consider the amount of carbonate

species which can be expected during DMFC operation. Methanol influences the equilibrium constant of the gas liquid interaction between carbon dioxide and the solution, and it impacts the dissociation of the carbonate system species. Therefore, a comparison of Henry's law constants with and without methanol influence will be given subsequently.

Refs. [11,10] investigated a vast set of experimental data for Henry's law constants in pure water systems. They present temperature dependent correlations valid for atmospheric pressure. Ref. [13] experimentally determined the impact of methanol concentration on Henry's law constants for methanol water solutions with CO_2.

According to Fig. B.1 the obtained curves from Refs. [11,10], Henry's law constant decreases linearly with decreasing temperatures below the maximal expected temperatures in the DMFC system of 353 K. Besides, it can be seen that methanol decreases Henry's law constant which consequently enhances CO_2 dissolution according to Equation (1). Methanol molar fractions of not more than $x_{Me} \approx 0.02$ and temperatures below 353 K are expected for the here considered portable autonomous DMFC system. No significant difference of Henry's law constants is observed in this region. This implies that methanol influence on the carbonate system in a DMFC system can be neglected for simulation and the constants for pure water are used in this work.
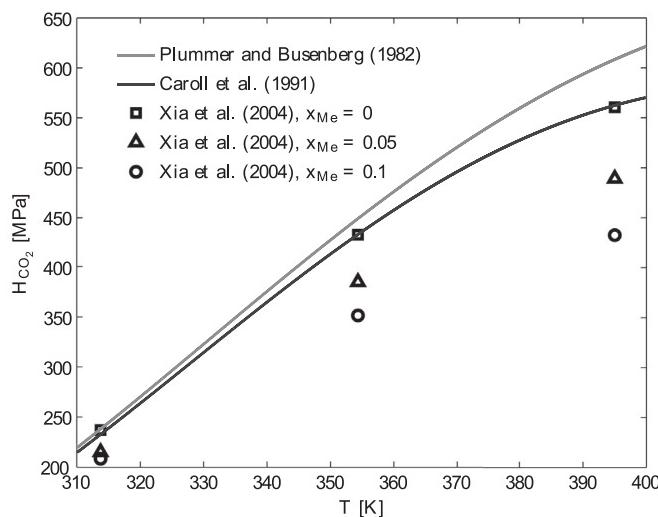

Fig. B.1. Comparison of Henry's law constant H_{CO_2} as function of temperature from $T = 310$ K to 400 K by Ref. [11] (light gray line) and [10] (dark gray line), together with the influence of methanol molar fraction with data by Ref. [13] (black square, triangle and circle marker, respectively).

Nomenclature

Latin symbols

c	concentration (mol l^{-1})
D	column diameter (m)
DIC	total dissolved inorganic carbon concentration (mol l^{-1})
F	volume flow (m^3 s^{-1})
F	Faraday constant (96485.309(23) A s mol^{-1})
H	Henry's law constant, unit depending on used definition
I	current (A)
k	water drag coefficient (−)
K_{a1}	equilibrium constant (mol l^{-1})
K_{a2}	equilibrium constant (mol l^{-1})
K_W	equilibrium constant for ion product of water (mol^2 l^{-2})
L	column length (m)
N_{cell}	number of fuel cells in a stack (−)

$\dot{n}$	molar flow (mol s^1)
M	molar mass kg mol^{-1}
p	pressure (MPa)
p'	partial pressure (MPa)
q	anion concentration in the resin phase (mol l^{-1})
Q	anion exchange capacity (mol l^{-1})
t	time (s)
T	temperature (K)

Greek symbols

ε	inter particle porosity (−)
λ	stoichiometry factor (−)
ρ	density (kg m^{-3})

Subscripts

AIXC	anion exchanger
atm	physical value at atmospheric conditions
a1	regarding the dissociation of dissolved carbon dioxide
a2	regarding the dissociation of hydrogen carbonate
cell	parallel connected single cells in a fuel cell stack
cool	regarding the cooler in the DMFC system
IE	regarding anion exchange or anion exchanger
in	physical value at inlet
FC	fuel cell
feed	fed to the anode compartment
Me	methanol
need	needed for stoichiometric yield
out	physical value at outlet
prod	produced amount of the physical value
reaction	lost due to the electrochemical reaction at anode
ret	implying anion retention
total	total physical value
xover	crossover from anode to cathode side

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